

Remote optical sensing instrument monitoring to demonstrate compliance with short-term exposure action limits during cleanup operations at uncontrolled hazardous waste sites[☆]

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Abstract

Remote optical sensing (ROS) is an emerging analytical technique. ROS provides the capability to remotely monitor and measure trace atmospheric gases by transmitting a beam of radiation across a parcel of air several hundred meters in length (e.g., open-path Fourier transform infrared spectroscopy). The information gained from these measurements can be used to calculate emission rates from sources, which can be modeled to determine downwind air quality impacts.

Traditionally, two monitoring methods were available to estimate air quality impacts: receptor measurements and source measurements. Receptor measurements are air monitoring or sampling methods that directly determine concentrations at downwind locations of concern (e.g., absorbent tubes collected at a school). Source measurements are air monitoring or sampling at or immediately downwind of a source to determine an emission rate (e.g., stack sampling at a facility). This emission rate is then used for estimating concentrations at downwind locations of concern.

The path-integrated approach has been utilized at Superfund sites to examine source emission impacts during full-scale remediation operations and during pilot-scale studies. The emission rates for the various compounds were modeled to determine if health-based action levels for the targeted compounds were exceeded at designated distances downwind of the monitoring. Utilization of ROS during these types of operations provided near real-time data to demonstrate compliance with short-term exposure action limits. The data were also used to

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determine the overall daily average fence line concentration and compare it with longer-term, exposure-based action limits.

Keywords: Remote optical sensing; OP-FTIR; OP-UV; Cleanup operations

1. Introduction

Remote optical sensing (ROS) is an emerging analytical technique. ROS provides the capability to remotely monitor and measure trace atmospheric gases by transmitting a beam of radiation across a parcel of air several 100 m in length [1]. The information gained from these measurements can be used to calculate emission rates from sources, which can be modeled to determine downwind air quality impacts. This paper will briefly describe (1) the general theory of ROS and the subsequent emission rate determination process, (2) an example of the calculations employed and (3) a discussion of a Superfund site case study using this technique to monitor short-term exposure action limits.

Traditionally, two monitoring methods were available to estimate air quality impacts: receptor measurements and source measurements. Receptor measurements are air monitoring or sampling methods that directly determine concentrations at downwind locations of concern. Source measurements are air monitoring or sampling at or immediately downwind of a source to determine an emission rate. This emission rate is then used for estimating concentrations at downwind locations of concern.

The advantage of the receptor measurement method is its ability to provide actual measured data and data for specific sensitive receptor locations. The disadvantages of the receptor measurement method are the following: (1) it is impractical for assessing the magnitude and spatial extent of the air quality impacts; (2) it is not well suited for exposure assessments; and (3) it frequently provides inadequate detection limits. The advantages of the source measurement method are that this method provides a cost-effective means of assessing the magnitude and spatial extent of air quality impacts and that the method is well suited for exposure assessments. The disadvantages of the source measurement method are the following: (1) it requires accurate estimation of emission rates; (2) it relies upon mathematical simulation of atmospheric transport and dispersion; and (3) it requires detailed logistical planning of observations of meteorology concurrent with air measurements.

2. General theory

In an unistatic configuration, the ROS transmitter and receiver are collocated and a retroreflector is used to reflect the transmitted radiation back to the receiver. The molecules in the beam's path absorb some of the radiation at certain wavelengths, resulting in the reduction of the intensity of the beam at that wavelength. The ratio of the measured intensities, the intensity with molecular absorption to the intensity

without molecular absorption, is defined as the transmittance [2] (Eq. (1)).

$$T(\nu) = \frac{I(\nu)}{I_0(\nu)} = \exp(-A(\nu)), \quad (1)$$

where $T(\nu)$ is the transmittance of the beam at a designated wavelength, $I(\nu)$ is the intensity of the beam with molecular absorbance at a designated wavelength, $I_0(\nu)$ is the intensity of the beam with no molecular absorbance at a designated wavelength and $A(\nu)$ is the absorbance of the beam at a designated wavelength.

The absorption is related to the concentration of the absorbing gas by the Beer–Lambert–Bouguer (BLB) law (Eq. (2)):

$$A(\nu) = \alpha_m(\nu) CL, \quad (2)$$

where $A(\nu)$ is the absorbance of the beam at a designated wavelength, $\alpha_m(\nu)$ is the instrument-independent molecular absorption coefficient associated with the collision-broadened absorption spectra of gases under standard atmospheric conditions at a designated wavelength, C is the compound concentration, ppmv, and L is the pathlength of the radiation through the gas, m.

I , I_0 , A , and α_m are functions of the radiation frequency, ν , which is proportional to the reciprocal of the wavelength. In the second equation, the absorbance $A(\nu)$ is proportional to the concentration-pathlength product, CL . The proportionality constant is the molecular absorption coefficient $\alpha_m(\nu)$, which is unique for each molecule and thus is the source of the unique “fingerprint” shapes of the absorption spectra of the different molecules. These absorption features also have temperature and pressure (altitude) dependencies. The infrared (IR) spectral region is 3–13 μm and the ultraviolet (UV) spectral region is 0.24–0.68 μm .

Gaseous contaminant concentrations are generally reported in units of mass of contaminant per volume of gas, such as milligrams per cubic meter (mg/m^3), or volume of contaminant per volume of gas, such as parts per million by volume (ppmv) or parts per billion by volume (ppbv). Path-integrated concentrations, however, are typically reported in units of milligrams per square meter (mg/m^2) or ppm-meters (ppm-m). With an open-path system, the total contaminant burden is measured within the cylinder defined by the finite cross-sections of the light beam at each end and the length of the beam itself. The contaminant burden is then normalized to a pathlength of 1 m.

A coordinate system showing Gaussian distribution in the horizontal and vertical is illustrated in Fig. 1. The general equation for the ground-level concentration (continuous point source) [3, 4] is presented in Eq. (3).

$$X(x, y, z = 0, H) = \frac{Q}{\pi\sigma_y\sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right], \quad (3)$$

where X is the concentration, mg/m^3 , x is the downwind distance to a receptor, m, y is the crosswind distance to a receptor, m, z is the vertical distance to a receptor, m, H is the effective height of emission, m, Q is the uniform emission rate, mg/s , σ_y and σ_z are the

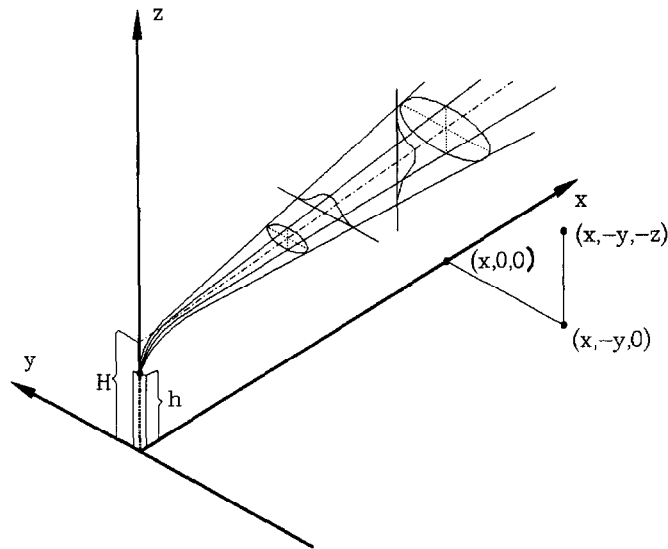


Fig. 1. Coordinate system showing the Gaussian distribution in the horizontal and vertical.

dispersion coefficients (horizontal and vertical, respectively), m , and u is the mean wind speed, m/s .

Integrating Eq. (3) with respect to "y" from negative to positive infinity results in Eq. (4). This equation can be used to determine emission rates from ground-level releases:

$$Q = \frac{\sqrt{2\pi}}{2} C(x) \sigma_z u, \quad (4)$$

where Q is the uniform emission rate, mg/s , $C(x)$ is the ground-level crosswind integrated concentration, mg/m^2 , σ_z is the dispersion coefficient (vertical), m , and u is the mean wind speed, m/s .

3. Example calculations

The benzene emission rate from a small spill (point source) may be determined by monitoring downwind with the remote optical sensing instrumentation and measuring the ground-level crosswind integrated concentration. Using the meteorological data collected concurrently with the remotely sensed monitoring data, record the mean wind speed observed and calculate the stability class from the Pasquill-Gifford tables. Insert these values into Eq. (4) and multiply by the appropriate conversion factor for benzene, 3.25 mg/m^3 per 1 ppmv, to achieve dimensional homogeneity. The

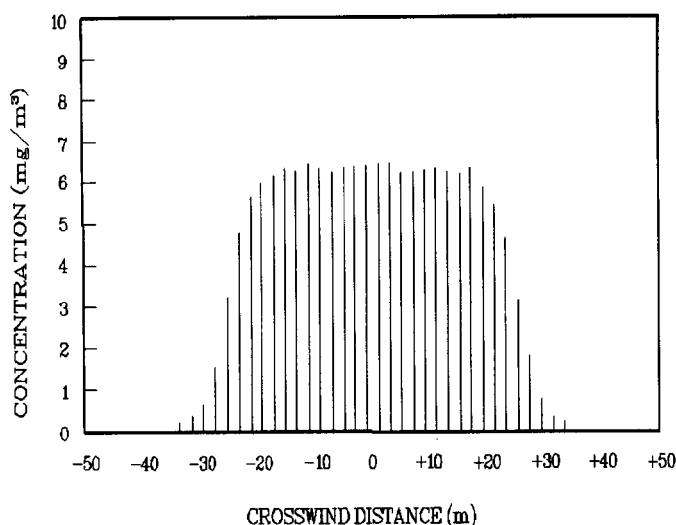


Fig. 2. PAL model to predict concentrations along the measurement path based on unity emission rate ($1 \text{ mg/m}^2\text{s}$) and actual wind speed and source configuration.

resulting equation becomes Eq. (5):

$$Q = \left(\frac{\sqrt{2\pi}}{2} \right) (10.8 \text{ ppm} - m) \frac{3.25 \text{ mg/m}^3}{1 \text{ ppm}} (2.1 \text{ m})(3 \text{ m/s}) = 277.1 \text{ mg/s.} \quad (5)$$

The benzene emission rate from a square waste lagoon (area source) measuring 2500 square meters may be determined by applying the following procedure. Monitor downwind with the remote optical sensing instrumentation and measure the ground-level crosswind integrated concentration. Using the meteorological data collected concurrently with the remote sensing monitoring, record the mean wind speed observed and calculate the stability class from the Pasquill–Gifford tables. Use the Point, Area, and Line Source (PAL) Model [5] to predict point concentrations along the measurement path based on unity emission rate ($1 \text{ mg/m}^2\text{s}$), actual wind speed, and source configuration (Fig. 2). By using an appropriate numerical technique such as the parabolic approximation (Simpson's Rule) (Eq. (6)), integrate the function:

$$\int_a^b f(x) dx \approx \frac{1}{3} \Delta x (y_0 + 4y_1 + 2y_2 + 4y_3 + 2y_4 + 4y_5 + \dots + 2y_{n-2} + 4y_{n-1} + y_n) \\ = 310.62 \text{ mg/m}^2 \quad (6)$$

After modeling with unity emissions, the estimated area emission rate can be calculated by taking the ratio of the modeled and measured results. The measured crosswind integrated concentration at $10.8 \text{ ppm}\cdot\text{m}$ is converted to 35.1 mg/m^2 by multiplying it by the appropriate factor to ensure dimensional homogeneity. The ratio

is established according to the following (Eq. (7)):

$$35.1 \frac{\text{mg/m}^2}{Q} = 310.62 \frac{\text{mg/m}^2}{1 \text{ mg/m}^2 \text{ s}}, \quad (7)$$

$$Q = 0.113 \frac{\text{mg}}{\text{m}^2 \text{ s}}.$$

To determine the emission rate of the entire lagoon, the emission rate per square meter is multiplied by the lagoon area (Eq. (8)):

$$Q = 0.113 \frac{\text{mg}}{\text{m}^2 \text{ s}} (2500 \text{ m}^2) = 282.5 \text{ mg/s}. \quad (8)$$

The ratio technique can also be used to estimate emission rates from either point sources or area sources. Use of the ratio technique requires no assumptions about the nature of the plume dispersion. The ratio technique is conceptually very simple to implement. The approach is to release an appropriate tracer at a known, controlled flow rate from locations that adequately simulate the source geometry. Both SF₆ and CF₄ are good tracers for infrared monitoring. Assuming that the tracer and source plumes are fully contained by the downwind beam, the following ratio applies (Eq. (9)):

$$C/Q = C_T/Q_T, \quad (9)$$

where C is the ground-level crosswind-integrated concentration of contaminant at distance x , mg/m², C_T is the ground-level crosswind-integrated concentration of tracer at distance x , mg/m², Q is the uniform emission rate of contaminant, mg/s and Q_T is the uniform emission rate of tracer, mg/s.

The equation simply states that the ratio of the path-integrated concentration of the contaminant to its emission rate is equal to the ratio of the path-integrated concentration of the tracer to its emission rate. It is important to note that all concentrations must be expressed in units of g/m² or mg/m². Use of ppm-m units will yield erroneous results because molecular weights are not accounted for. Rearranging the equation and solving for Q yields (Eq. (10)):

$$Q = Q_T C / C_T \quad (10)$$

4. Superfund site case study

The path-integrated approach has been utilized at Superfund sites to examine source emission impacts during full-scale remediation operations and during pilot-scale studies. The emission rates for the various compounds were modeled to determine if health-based action levels for the targeted compounds were exceeded at designated distances downwind of the monitoring. Utilization of remote optical sensing during these types of operations provided near real-time data to demonstrate compliance with short-term exposure action limits. The data were also used to

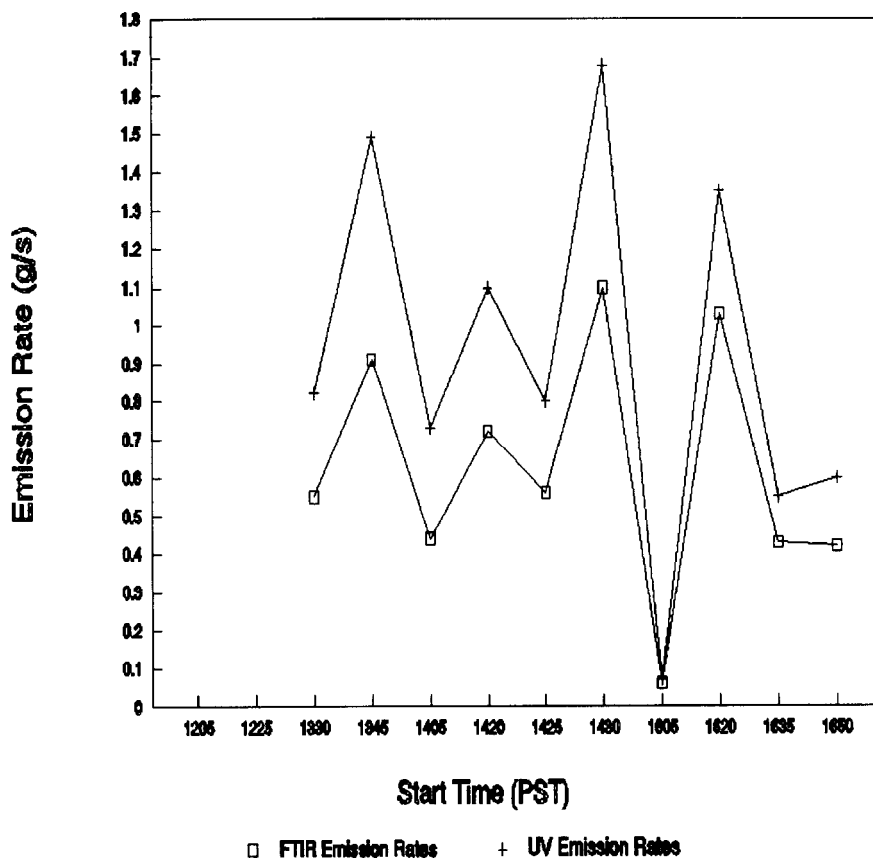


Fig. 3. SO₂ emission rates for day 10 of the California monitoring study.

determine the overall daily average fence line concentration and compare it with longer-term, exposure-based action limits.

At a site in California, both the open-path Fourier transform infrared (OP-FTIR) spectrometer and the open-path ultraviolet (OP-UV) spectrometer were employed to examine the source emissions during excavation activities. Sulfuric acid bearing petroleum refining and production wastes, which had been deposited in subsurface trenches along backyard fence lines of the houses in the neighborhood, were being excavated during a pilot-scale operation. The remote optical systems were also used to measure emission rates during vapor-suppression activities, which utilized water mist, foam, and oxidizing solutions. Fig. 3 provides a graph of emission rates versus time for one of the excavation operations. The agreement between the instruments is very good and therefore, provides us with confidence when calculating their impact downwind.

Immediately after the source's emission rate was estimated, the PAL model was applied to evaluate the effective off-site exposures. The PAL model was used because

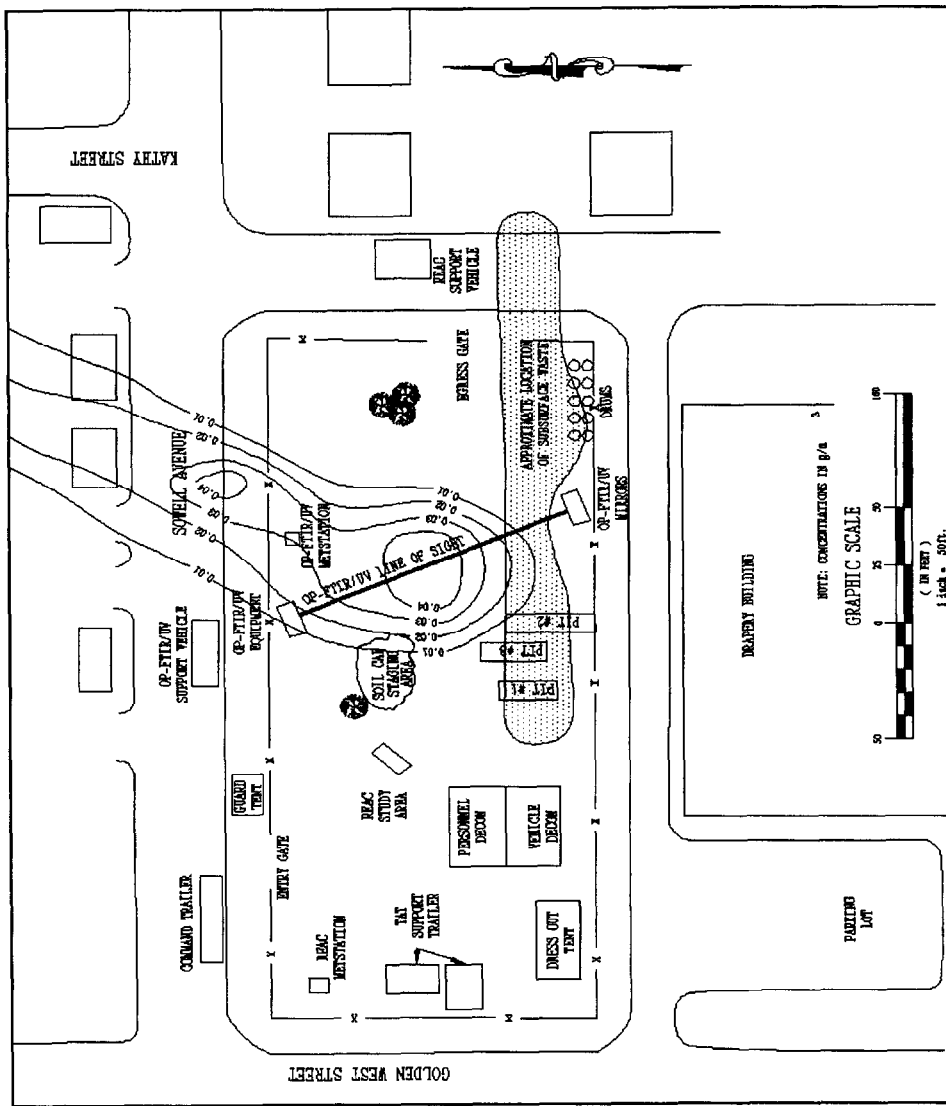


Fig. 4. Maximum 1 h concentrations of SO₂ at the California site on March 1992.

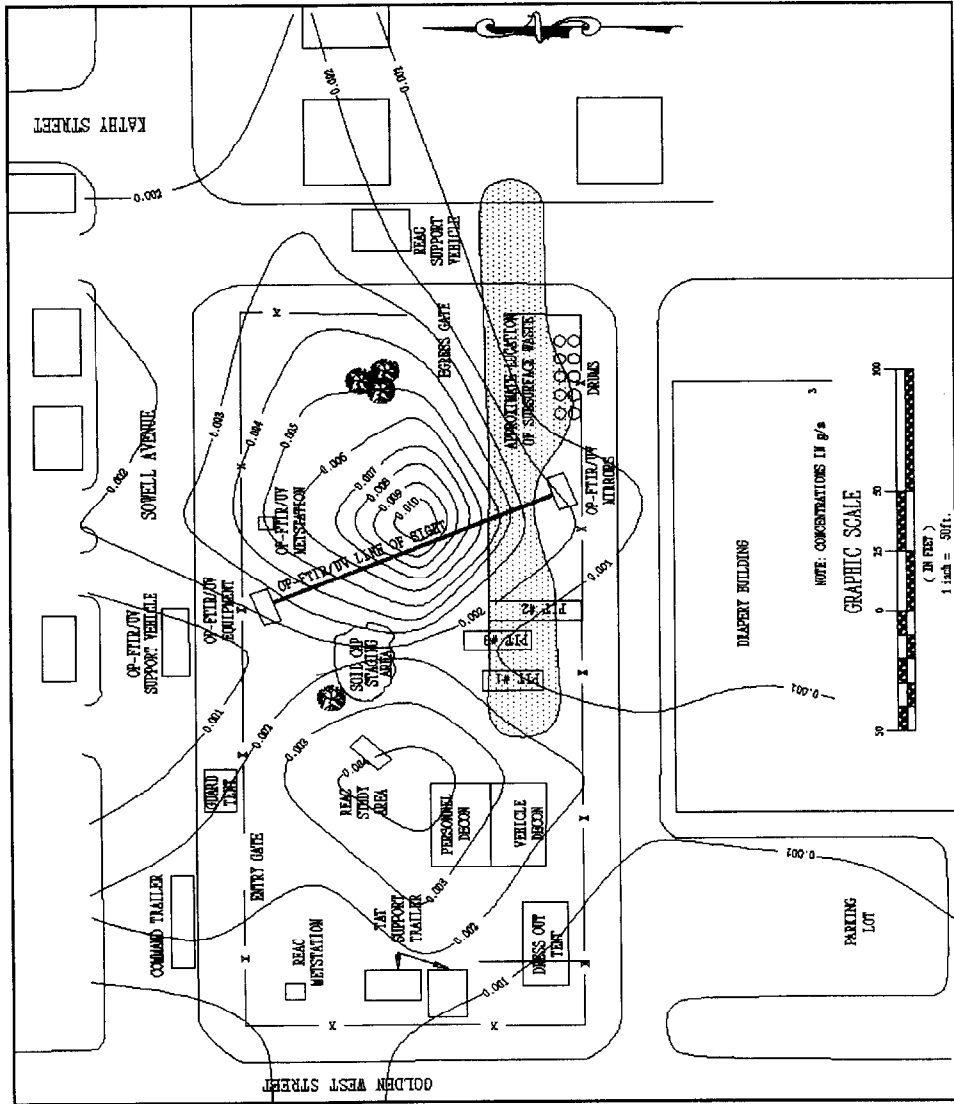


Fig. 5. Eight-hour concentrations of SO₂ at the California site on March 1992.

it provides an iterative line-source scheme to predict downwind concentrations from area sources. It produces the most reliable results of all of the EPA accepted area source models [6]. The emission rate was used in the model with the meteorological conditions that were observed on site. An example of the estimated downwind concentrations for the episode with the largest impact is provided below. The wind originated from the southwest during the episode. A graphical depiction of the ambient concentrations within the predicted plume is provided in Fig. 4. The maximum (1 h) off-site concentration predicted for SO₂ was 20 ppm (50 mg/m³); this was below the 100 ppm Immediately Dangerous to Life and Health threshold but above the 2 ppm Threshold Limit Value-Time Weighted Average (TLV-TWA), an acceptable exposure level for an 8 h period. The figure also illustrates the capture of the plume by the ROS.

These results are significant because the residents were in very close proximity and the emission rates observed approached the established short-term exposure action limits. The use of the near real-time monitoring allowed the on-site coordinator to make changes to remediation operations as extenuating circumstances were observed and avoid exceedance of the short-term exposure action levels.

The meteorological conditions for the duration of the study were evaluated to provide a typical 8 h exposure. The model results for SO₂ dispersion during spring time like conditions are provided in Fig. 5. As illustrated in the figure, the prevailing impact of the emissions is to the east of the site. The highest typical eight-hour average concentration at the receptors is about 1.3 ppm (3.4 mg/m³), below the TLV-TWA. However, this value indicates that continual monitoring would be important to ensure that the TLV-TWA is not exceeded for any 8 h period.

5. Conclusion

ROS is an emerging analytical technique that will be of great value in monitoring air quality impacts. ROS is capable of providing reliable, important data during cleanup operations at Superfund sites. This technique also provides an ability to determine emission rates from point, line and area sources in a timely (near real-time), cost effective manner. Application of this technique reduces the impact that site activities may have before significant exposure is realized. Engineering decisions can be instituted during activities to reduce the emissions without discontinuance of work; thus reducing both the short and long-term exposure while maintaining the budgeted time lines.

Furthermore, as the Clean Air Act becomes implemented, remote optical sensing will provide a method to monitor for polar compounds without consideration for the collection, storage, extraction, and analysis problems. It is important to understand the advantages and disadvantages of each type of monitoring. The advantages of the point concentration approach are the following: it provides a means for direct comparison of observed versus predicted concentrations at specific locations, and is suitable for directly assessing model accuracy and reliability in predicting short-term peak concentrations. The disadvantages of the point concentration approach are that

the results are not representative due to the inherent random nature of turbulence, and the method is impractical for assessing total model performance. The advantages of the path-integrated approach are: it handles inherently random nature of turbulence; it yields data that can be directly compared with model predictions; and it provides data, which can be used to directly determine site-specific vertical dispersion coefficients. The disadvantages of the path-integrated approach are that it does not provide means for direct comparison of observed versus predicted concentrations at specific locations, and it is not suitable for directly assessing model accuracy and reliability in predicting short-term peak concentrations.

The type of monitoring approach preferred depends on the data quality objectives of the study. Point monitoring is preferred for receptor measurements, since it provides actual measured data at sensitive receptor locations. Path-integrated monitoring is preferred for source measurements, since it accurately relates source emissions.

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